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POLYAMIDE, PRODUCTION METHOD AND BONDING METHOD THEREOF, AND METHOD
FOR PRODUCING RELIEF PRINTS

[Poriamido, Sono Seizoho, Oyobi Setchakuho Narabini Rerifu
Insatsubutsu No Seizoho]

Manfred Drawert, et al.

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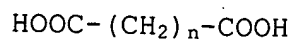
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INVENTORS	(72): DRAWERT, MANFRED; KRASE, HORST
APPLICANT	(71): SCHERING AKTIENGESELLSCHAFT
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[Claims]

/2*

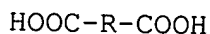
[Claim 1] A polyamide prepared by condensation of:

(A1) a minimum of one of the aliphatic dicarboxylic acids represented by the general formula below:



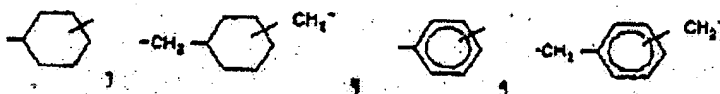
(wherein n is from 4 to 11);

(A2) a minimum of one of the acids represented by the general formula below:



(wherein the group R is

[Chem. 1]



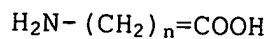
and wherein the ratio of A1 to A2 ranges from 1:0.1 to 1:2 mols);

optionally (A3) a saturated monocarboxylic acid in an amount of up to 0.1 mol, based on the amount of the carboxylic acid of A1;

(B) a minimum of one diamine selected from a group consisting of 1,6-diaminohexane, 1,5-diamino-2-methyl-pentane, 2,4,4(4,4,2)-trimethyl-1,6-diaminohexane, 1,9-diaminononane, and 1,12-diaminododecane (wherein the ratio of the components A1 plus A2 to B is essentially equivalent based on amino groups and acid groups); and

(C) a minimum of one of the aminocarboxylic acids represented by the general formula below:

* Claim and paragraph numbers correspond to those in the foreign text.



(wherein n is from 5 to 11) or lactams thereof (wherein from 0.5 to 1.5 mols of aminocarboxylic acid or lactam is used per mol of carboxyl acid [sic] of the acids named under A)

by a known method at a temperature of from 200 to 280 °C, optionally employing commonly used amidation catalysts, at a vacuum of less than 100 millibars applied at the end of the reaction.

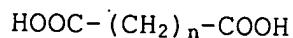
[Claim 2] The polyamide stated in Claim 1, wherein ε-aminocarboxylic acid and/or caprolactam are used as the aminocarboxylic acid of C.

[Claim 3] The polyamide stated in Claim 1, wherein dimerized fatty acid is substituted for up to less than 0.05 mol of the co-dicarboxylic acid of A2.

[Claim 4] The polyamide stated in Claim 1, wherein 1.0 mol of sebacic acid is used as component A1, from 0.3 to 0.8 mol of isophthalic acid is used as component A2, dimerized fatty acid is optionally substituted for up to less than 0.05 mol of the isophthalic acid, from 1.3 to 1.6 mols of 1,6-diaminohexane is used as component B, and from 2.6 to 3.6 mols of caprolactam is used as component C.

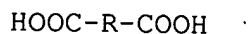
[Claim 5] A process for the preparation of a polyamide comprising polycondensation of

(A1) a minimum of one of the aliphatic dicarboxylic acids represented by the general formula below:



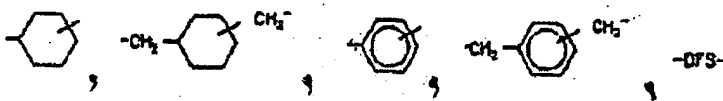
(wherein n is from 4 to 11);

optionally [sic] (A2) a minimum of one of the acids represented by the general formula below:



(wherein the group R is

[Chem. 2]

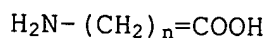


-DPS- representing the residue of dimerized fatty acids, and wherein the ratio of A1 to A2 ranges from 1:0.05 to 1:2.0 mols and preferably is 1:0.5 mole);

optionally (A3) a saturated monocarboxylic acid in an amount of up to 0.1 mol, based on the amount of the carboxylic acid of A1;

(B) a minimum of one diamine selected from a group consisting of 1,6-diaminohexane, 1,5-diamino-2-methyl-pentane, 2,4,4(4,4,2)-trimethyl-1,6-diaminohexane, 1,9-diaminononane, and 1,12-diaminododecane (wherein the ratio of the components A1 plus A2 to B is essentially equivalent based on amino groups and acid groups); and

(C) a minimum of one of the aminocarboxylic acids represented by the general formula below:



(wherein n is from 5 to 11) or lactams thereof (wherein from 0.5 to 1.5 mols of aminocarboxylic acid or lactam is used per mol of carboxyl acid [sic] of the acids named under A)

by a known method at a temperature of from 200 to 280 °C, optionally employing commonly used amidation catalysts, at a vacuum of less than 100 millibars applied at the end of the reaction.

[Claim 6] The process stated in Claim 5, wherein 1.0 mol of sebacic acid is used as component A1, 0.5 mol of isophthalic acid is used as component A2, dimerized fatty acid is optionally substituted for up to 0.05 mol of the isophthalic acid, 1.5 mols of 1,6-diaminohexane is used as component B, and from 3 mols of caprolactam is used as component C.

[Claim 7] The process stated in Claim 5, wherein the components A through C and their ratios are chosen so that the resulting polyamide has a melting point between 90 and 150 °C.

[Claim 8] The process stated in any of Claims 5 through 7, wherein the components A through C and their ratios are chosen so that the viscosity, as determined at 220 °C, is in the range of from 10 to 150 Pa·s.

[Claim 9] A method for bonding cardboard, paper, fabrics formed from natural fibers and/or synthetic fibers, such as knitted/woven cloth and fiber tapestries, metal, or glass, wherein the polyamide stated in any one of Claims 1 through 4 is used.

[Claim 10] A method for producing relief prints, wherein the polyamide stated in any one of Claims 1 through 8 is used.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application] The present invention relates to polyamides based on mixtures of acids, amines, and aminocarboxylic acids and to their use particularly in the production of non-yellowing relief printing which, moreover, shows good adhesion to various substrates.

[0002]

[Related Art] The relief decoration of organic and inorganic substrates has long been known.

[0003] The original technique of applying relief-like printing to paper or cardboard for, for example, book covers, promotional articles, postcards, business cards, wrappers, etc., consists in executing the raised or sunk embossing with engraved plates or with printing type on printing presses with or without color transfer. In the process, the image to be printed is printed in one or more colors in one or more passes and then embossed in relief.

[0004] In recent years, a modification of this technique has been steadily gaining ground. Here, an image is still printed on the substrate, but the embossing step is dispensed with. The relief is produced by coating the image with a thermoplastic synthetic resin.

[0005] Technically, the process that prints the substrate by the offset method with the printing inks commonly used therewith is advancing. Immediately thereafter, a finely pulverized thermoplastic resin is sprinkled on the surface of the printing while it is still wet and tacky. The excess powder is removed by suction from the

unprinted, and therefore nontacky, areas. In a heat treatment that follows this step, the resin is heated to a temperature above its melting point.

[0006] In this case, the thermoplastic resin must meet a number of requirements, the most important of these being that it should have no color of its own, or as little as possible, and that it should be grindable to a fine powder that will not block even under the conditions of use and thus remains free flowing.

[0007] The polyamide resins based on dimerized fatty acids and ethylene diamine used to date for this purpose do meet several of these requirements but do not fully satisfy others, such as the number of colors [sic], resistance to discoloration, and, in particular, adhesion to metal and glass. Moreover, the fatty acids that are hydrogenated to produce these polyamide resins must have iodine numbers under 10, and, during the condensation, even minor amounts of atmospheric oxygen will result in an appreciable deterioration of the number of colors [sic].

[0008]

[Problems that the Invention Intends to Solve] The present invention intends to overcome these drawbacks of the prior art and to provide resins that, in contrast to the resins used up to now, which produce a smooth and glossy surface, impart to relief prints an effective, matte surface with a grainy structure that, at the same time, is scratch-resistance.

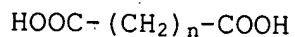
[0009] These resins should also provide good adhesion to various substrates, particularly to paper, cardboard, metal, and glass, good flexibility, compatibility with the background color, and nontacky surfaces.

[0010]

[Means for Solving the Problems] From the specification of German published patent application No. 3510415 are known polyamides that are based on a hydrogenated dimerized fatty acid, optionally a co-dicarboxylic acid, a specially matched combination of straight-chain and branched short-chain monocarboxylic acids, and an amine mixture of ethylene diamine and hexamethylene diamine. While these products actually show an improvement with respect to surface properties, number of colors, and discoloration resistance, their preparation still requires that dimerized fatty acids be hydrogenated to the point where the iodine number is not higher than 25. Relief prints made with these resins show a smooth and glossy surface.

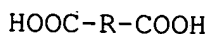
[0011] An object of the present invention is a polyamide prepared by condensation of:

(A1) a minimum of one of the aliphatic dicarboxylic acids represented by the general formula below:



(wherein n is from 4 to 11);

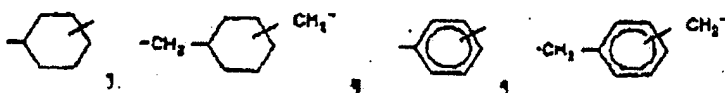
(A2) a minimum of one of the acids represented by the general formula below:



(wherein the group R is

[0012]

[Chem. 3]

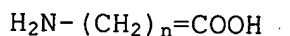


[0013] and wherein the ratio of A1 to A2 ranges from 1:0.1 to 1:2 mols);

(A3) a saturated monocarboxylic acid in an amount of up to 0.1 mol, based on the amount of the carboxylic acid of A1;

(B) a minimum of one diamine selected from a group consisting of 1,6-diaminohexane, 1,5-diamino-2-methyl-pentane, 2,4,4(4,4,2)-trimethyl-1,6-diaminohexane, 1,9-diaminononane, and 1,12-diaminododecane (wherein the ratio of the components A1 plus A2 to B is essentially equivalent based on amino groups and acid groups); and

(C) a minimum of one of the aminocarboxylic acids represented by the general formula below:



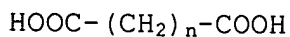
(wherein n is from 5 to 11) or lactams thereof (wherein from 0.5 to 1.5 mols of aminocarboxylic acid or lactam is used per mol of carboxyl acid [sic] of the acids named under A)

by a known method at a temperature of from 200 to 280 °C, optionally employing commonly used amidation catalysts, at a vacuum of less than 100 millibars applied at the end of the reaction.

[0014] A further object of the present invention is characterized in that 1.0 mol of sebacic acid is used as component A1, from 0.3 to 0.8 mol of isophthalic acid is used as component A2, dimerized fatty acid is optionally substituted for up to 0.05 mol of the isophthalic acid, from 1.3 to 1.8 mols of 1,6-diaminohexane is used as component B, and from 2.6 to 3.6 mols of caprolactam is used as component C.

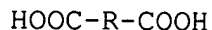
[0015] Yet another object of the present invention is a process for the preparation of a polyamide comprising polycondensation of:

(A1) a minimum of one of the aliphatic dicarboxylic acids represented by the general formula below:



(wherein n is from 4 to 11);

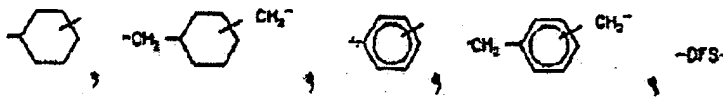
optionally [sic]. (A2) a minimum of one of the acids represented by the general formula below:



(wherein the group R is

[0016]

[Chem. 4]

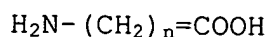


[0017] -DPS- representing the residue of dimerized fatty acids, and wherein the ratio of A1 to A2 ranges from 1:0.05 to 1:2.0 mols and preferably is 1:0.5 mole);

(A3) a saturated monocarboxylic acid in an amount of up to 0.1 mol, based on the amount of the carboxylic acid of A1;

(B) a minimum of one diamine selected from a group consisting of 1,6-diaminohexane, 1,5-diamino-2-methyl-pentane, 2,4,4(4,4,2)-trimethyl-1,6-diaminohexane, 1,9-diaminononane, and 1,12-diaminododecane (wherein the ratio of the components A1 plus A2 to B is essentially equivalent based on amino groups and acid groups); and

(C) a minimum of one of the aminocarboxylic acids represented by the general formula below:



(wherein n is from 5 to 11) or lactams thereof (wherein from 0.5 to 1.5 mols of aminocarboxylic acid or lactam is used per mol of carboxyl acid [sic] of the acids named under A)

by a known method at a temperature of from 200 to 280 °C, optionally employing commonly used amidation catalysts, at a vacuum of less than 100 millibars applied at the end of the reaction.

[0018] A further object of the present invention is the use of the polyamide resins of the present invention in the production of relief prints.

[0019] Examples of the dicarboxylic acids of A1 used in accordance with the present invention are straight-chain dicarboxylic acids having from 6 to 13 carbon atoms, such as adipic acid, suberic acid, azelaic acid, brassylic acid, and preferably sebacic acid and decamethylene dicarboxylic acid. If desired, shorter-chain

dicarboxylic acids, such as adipic acid or pimelic acid may also be used.

[0020] As the dicarboxylic acid described in A2, 1,4 (1,3)-cyclohexane dicarboxylic acid, 1,4 (1,3)-cyclohexane diacetic acid, terephthalic acid, 1,4 (1,3)-phenylene diacetic acid, and particularly isophthalic acid are used.

[0021] By dimerized fatty acids are meant commercial polymerized fatty acids that have iodine numbers ranging from about 100 to 130 and whose dimeric fatty acid content has been increased by commonly used processes to from about 85 to 100 %.

[0022] The iodine number is determined by methods commonly employed in practice and is expressed in grams of iodine per 100 grams of substance.

[0023] The polymerized fatty acids can be prepared by the usual processes (see, for example, U. S. patents 2,482,761 and 3,256,304) from unsaturated natural and synthetic monobasic fatty acids having from 12 to 22, preferably 18, carbon atoms.

[0024] Typical commercial polymeric fatty acids have approximately the following composition prior to distillation:

Monomeric acids	5 to 15 % by weight
Dimeric acids	60 to 80 % by weight
Tri- and higher-polymeric acids	10 to 35 % by weight

After distillation, the dimeric acid fraction should be nearly free of monocarboxylic acids, and the proportion of trimerized and higher-polymerized fatty acids should be 1 % by weight or less.

[0025] Both the distilled and undistilled fatty acids can be hydrogenated by known processes to lower the iodine number, preferably to the range from 10 to 40. In accordance with the present invention, hydrogenated dimerized fatty acids with iodine numbers between 10 and 15 and a dimeric fatty acid content of not less than 90 % by weight are preferred.

[0026] The composition of the fatty acids is determined by the usual gas-liquid chromatography (GLC) techniques, with the specification of the dimer content including, in addition to the dimerized fatty acids, the minor amounts of completely or partially decarboxylated dimerization products that are inevitably formed in the dimerization process.

[0027] The ratio of the carboxylic acids A1 to A2 should range from 1:0.1 to 1:2 mols, preferably from 1:0.3 to 1:0.8 mols, and will depend on the particular components A1 and A2, and, in some measure, on the amount and nature of component C, that is, the amino acid or lactam. For the preparation of particularly lightfast polyamides, it is, in accordance with the present invention, that no dimerized fatty acid, or not more than 0.05 mol, be used.

[0028] For regulation of the molecular weight, monocarboxylic acids having up to 18 carbon atoms may be used, the highly saturated

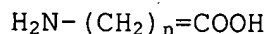
and straight-chain acids having from 16 to 20 carbon atoms, such as palmitic acid and stearic acid in particular, being preferred in accordance with the present invention. These acids are preferably used in amounts of from 0.05 to 0.1 mol, based on the carboxylic acids of A1.

[0029] The molecular weight may also be regulated with excess acid or amine. However, since free carboxyl groups or amino groups are then present in the molecule, this approach is less preferred in accordance with the present invention.

[0030] As the amino component, it is advantageous to use 2-methyl-1,5-diaminopentane and a mixture of isomers of 2,4,4(4,4,2)-trimethyl-1,6-diaminohexane, 1,9-diaminononane, and 1,12-diaminododecane concomitantly with 1,6-diaminohexane.

[0031] The ratio of the acid component A to the amino component B is approximately equivalent. The polyamides preferably have amine and acid values not higher than 10, and the sum of the acid and amine values should not exceed 10, either.

[0032] The amino acids of C that may also be used in accordance with the present invention have the general formula:



(wherein n is 5 to 11) or their lactams, preferably with n = 5.

[0033] From 0.5 to 1.5 mols, preferably 1.0 mol, of amino acid or lactam should be used per mol of carboxyl groups of the dicarboxylic acids named under A.

[0034] If necessary, minor amounts of commonly used monocarboxylic acids, preferably of stearic acid, may be used for regulation of the molecular weight or of the viscosity.

[0035] The polyamide resins used in accordance with the present invention can be ground into a powder that will remain free-flowing even under coating conditions, possible with the concurrent use of antiblocking agents, such as stearates, Aerosil, or the like. The particle size of the powder may be varied as required and will range from 40 to 500 microns, preferably from 80 to 200 microns.

[0036] The melting point of the resins is adapted to the actual requirements. It is sufficiently low to prevent impairment of the substrate or of the background lacquer by the complete melting temperatures, yet high enough for no blocking to occur even at application temperatures.

[0037] The preferred melting range (as measured by the ring and ball method) is from about 90 to 150 °C, preferably from 100 to 140 °C.

[0038] Furthermore, the resins have a narrow melting range, which makes it possible to rapidly achieve freedom from tackiness and blocking during the cooling stage, which follows the melting stage. This is a very important factor in attaining short cycle times.

[0039] The melt viscosities, measured uniformly at 220 °C with a rotary cone-plate viscometer as directed by its manufacturer, Haake Co., range from about 10 to 200 Pa·s, preferably, from 15 to 80 Pa·s, better yet, from 20 to 50 Pa·s.

[0040] The polyamide resins of the present invention, which are compatible with the background colors commonly used in this field, permit a combination of additional and novel properties and effects to be achieved in relief printing.

[0041] In contrast to the resins commonly used up to now, which provide a smooth, glossy, and delicate surface, the resins of the present invention impart to relief prints an effective, matte surface with a grainy texture or a fine-grained leather texture that has extraordinary scratch resistance.

[0042] In addition to good adhesion to the usual substrates, such as cardboard, paper, fabrics made of natural fibers and/or synthetic fibers, such as knitted/woven cloth and tapestries, the resins of the present invention have excellent adhesion to metal and glass.

[0043] The grainy texture further imparts sure-grip properties to containers so imprinted, such as bottles and jars for body-care agents used in the cosmetic industry.

[0044] Because of the negligible intrinsic color and high transparency of the polyamide resins of the present invention, shifts in hue of the subjacent color print do not occur, and these resins are substantially non-yellowing both during application and on exposure to ultraviolet radiation.

[0045] Testing of Polyamide Resins
Procedure A

The polyamide resins of Examples 1 to 22 obtained in accordance with the present invention were coarsely crushed, chilled with dry ice and/or liquid nitrogen, and ground cold in an impact mill (made by Alpine Co.). From the powder thus obtained, a size fraction of from 40 to 500 microns was then screened out by means of a set of screens. A black-pigmented high-viscosity offset ink was then applied by means of a simple manually operated printing press to the coated (smooth) side of a white light-weight cardboard, and, after 10 to 20 seconds' airing, the screened powder was sprinkled onto it. Because of the tacky character of the ink, an amount of powder sufficient for the formation of a textured surface adhered while the surplus material could readily be removed. The cardboard so prepared was then heated in a special powder-melting apparatus (a Konvexograph, made by Grafra Co.) with infrared rays (IR) from above, at a distance of 20 to 30 cm. After a retention time of about 5 to 10 seconds, highly scratch-resistant, grainy surface textures were obtained. Since the polyamide resins have virtually no intrinsic coloration and no tendency to yellow, no graying of the black color of the printing ink could be observed.

[0046] Procedure B

A variation of the application of a background color consists in first printing a polyamide resin lacquer capable of being reactivated, in the form of the desired designs, by gravure printing onto continuous sheets, such as a web of aluminum foil or the like. Unlike the offset ink referred to above, this specially formulated lacquer is

tack-free immediately after printing, and the aluminum foil wound into rolls after the printing operation can therefore be readily unwound. The foil or foil sections so unwound are heated shortly before the powder is sprinkled onto them. As a result, the imprinted lacquer becomes tacky and, because of its special formulation, remains tacky for from 3 to 10 seconds after cooling, with the powder sprinkled onto it adhering to the lacquer in the desired amount. The further melting process takes place as described in the foregoing.

[0047] Procedure C

Five centimeter-wide strips of a polyester/wool (55 %/45 %) substance were bonded. The polyamide powder had a particle size of from 300 to 400 μ . The application quantity was 20 g/m² of the substance.

[0048] The substance strips so treated were adhesive-bonded at temperatures of about 20 to 30 °C, which exceed [sic] the softening point of the polyamide adhesive, to two untreated substance strips. The bonding time was about 15 to 20 seconds, and the bonding pressure, 400 g/cm².

[0049] The bonded substance was completely immersed in a perchloroethylene bath, and, 30 minutes later, the peel strength was determined wet in conformity with DIN 53310.

[0050]

[Working Examples]

Preparation of Polyamide Resins

Example 1

In a 2-liter three-neck flask equipped with a stirrer, thermometer, and downward condenser, 202.0 g (1.0 mol) of sebacic acid (A_1), 83.0 g (0.5 mol) of isophthalic acid (A_2), 20.0 g (0.07 mol) of stearic acid (A_3), 339.0 g (3.0 mols) of caprolactam (C), 182.3 g (1.57 mols) of hexamethylene diamine (B), and 0.21 g of 85 % phosphoric acid (0.025 % by weight, based on the total weight of the ingredients) as a catalyst were mixed in a nitrogen ambience. In addition, 100.0 g of desalted water was added for better homogenization and heated over 2 hours to 240 °C. This temperature was maintained for 2 hours, a vacuum of 5 millibars being applied during the last 2 hours. This was followed by flushing with nitrogen, and the polyamide was then discharged. The polyamide obtained had a ring-and-ball softening point (DIN 52011) of 129 °C, a viscosity of 26.0 Pa·s at 220 °C (determined by means of the PK 401 W rotational viscometer as directed by its manufacturer, Haake Co. of Karlsruhe), an acid value of 3.9, and an amine value of 0.7.

[0051] By the working examples given in Table 1 below, similar products were obtained.

[0052] Here, the symbols have the following meanings:

AZ (amine value) = mg KOH/g of substance.

SZ (acid value) = mg KOH/g of substance.

R + B = Softening point, as determined by the ring-and-ball method (DIN 52011).

Viscosity = Viscosity, determined at 220 °C directly from the melt by means of the PK 401 W cone-plate viscometer as directed by its manufacturer, Haake Co. of Karlsruhe/Berlin.

Pripol (trademark) = Product name of Unichema International Co.

Pripol (trademark) 1009 = Hydrogenated polymerized fatty acid containing:

- 0.1 % monomeric fatty acid;
- 99.0 % dimeric fatty acid; and
- 1.0 % trimeric fatty acid

Pripol (trademark) 1013 = Polymerized fatty acid containing:

- 0.1 % monomeric fatty acid;
- 95.0 % dimeric fatty acid; and
- 5.0 % trimeric fatty acid

[0053]

[Table 1]

TABLE 1

	(a) 酸		(b) ジアミン		(c) 添加剤		AZ	SZ	R+B	粘度(d)
(e) 例	(f)モル量						°C		220 °C	Pa·s
1	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(k)	1.57	カプロラクタム (l)	3.0	0.7	3.9	129	26.0
	ステアリン酸(h)	0.07								
	イソフタル酸(i)	0.50								
2	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(k)	1.57	カプロラクタム (l)	3.0	0.5	2.6	110	100.0
	ステアリン酸(h)	0.07								
	Prilpol (j)(登録商標) 1009	0.50								
3	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(k)	1.57	カプロラクタム (l)	3.0	0.5	1.0	103	95.0
	ステアリン酸(h)	0.07								
	Prilpol (j)(登録商標) 1018	0.50								

Key: a) acid; b) diamine; c) additive; d) viscosity; e) example; f) quantity in mols; g) sebacic acid; h) stearic acid; i) isophthalic acid; j) (trademark); k) hexamethylene diamine; l) caprolactam

[0054]

[Table 2]

	(a) 酸		(b) ジアミン		(c) 添加剤		AZ	SZ	R+B	粘度(d)	
(e) 例	モル量(f)								°C	220 °C	Pa·s
4	セバシン酸(g)	0.90	ヘキサメチレン ジアミン(k)	1.55	カプロラクタム (l)	3.0	3.3	5.3	125	15.0	
	ステアリン酸(h)	0.05									
	Prilpol (登録商標)(j)	0.10									
	1009 イソフタル酸(i)	0.50									
5	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(k)	1.56	カプロラクタム (l)	3.0	3.0	6.0	126	24.0	
	ステアリン酸(h)	0.06									
	ジメチル(m) テレフタレート	0.50									
6	セバシン酸(g)	0.75	ヘキサメチレン ジアミン(k)	1.58	カプロラクタム (l)	3.0	0.8	2.3	126	29.0	
	ステアリン酸(h)	0.08									
	アジピン酸(n)	0.75			アミノウンデ カン酸(o)	1.5					

Key: a) acid; b) diamine; c) additive; d) viscosity; e) example; f) quantity in mols; g) sebacic acid; h) stearic acid; i) isophthalic acid; j) (trademark); k) hexamethylene diamine; l) caprolactam; m) dimethyl terephthalate; n) adipic acid; o) aminoundecanoic acid

[0055]

[Table 3]

	(a) 酸		(b) ジアミン		(c) 添加剤		AZ	SZ	R+B	粘度(d)
(e) 例	モル量(f)								°C	220 °C Pa·s
7	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(j)	1.56	カプロラクタム (k)	4.50	1.0	4.9	143	48.0
	ステアリン酸(h)	0.06								
	イソフタル酸(i)	0.50								
8	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(j)	2.07	カプロラクタム (k)	4.0	0.9	2.4	150	56.0
	ステアリン酸(h)	0.07								
	イソフタル酸(i)	1.00								
9	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(j)	3.10	カプロラクタム (k)	6.0	0.6	1.5	150	48.1
	ステアリン酸(h)	0.10								
	イソフタル酸(i)	2.00								
10	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(j)	1.55	カプロラクタム (k)	1.5	2.5	6.5	126	18.0
	ステアリン酸(h)	0.05								
	イソフタル酸(i)	0.50								

Key: a) acid; b) diamine; c) additive; d) viscosity; e) example; f) quantity in mols; g) sebacic acid; h) stearic acid; i) isophthalic acid; j) hexamethylene diamine; k) caprolactam

[0056]

[Table 4]

	(a) 酸		(b) ジアミン		(c) 添加剤		AZ	SZ	R+B	粘度(d)	
(e) 例	モル量 (f)								°C	220 °C	Pa·s
11	セバシン酸(g)	1.00	ヘキサメチレン- ジアミン (k)	3.10	カプロラクタム (l)	3.0	1.8	8.0	143		22.0
	ステアリン酸(h)	0.10									
	イソフタル酸(i)	2.00									
12	アジピン酸(j)	1.00	ヘキサメチレン ジアミン (k)	2.06	カプロラクタム (l)	2.0	2.1	8.0	133		26.0
	ステアリン酸(h)	0.06									
	イソフタル酸	1.00									
13	アジピン酸(j)	1.00	ヘキサメチレン ジアミン (k)	2.06	カプロラクタム (l)	4.0	1.4	5.8	143		31.0
	ステアリン酸(h)	0.06									
	イソフタル酸(i)	1.00									

Key: a) acid; b) diamine; c) additive; d) viscosity; e) example; f) quantity in mols; g) sebacic acid; h) stearic acid; i) isophthalic acid; j) adipic acid; k) hexamethylene diamine; l) caprolactam

[0057]

[Table 5]

	(a) 酸		(b)ジアミン		(c) 添加剤		AZ	SZ	R+B	粘度(d)
(e) 例	モル量(f)								°C	220 °C Pa·s
14	セバシン酸(g)	1.00	トリメチル ヘキサメチレン ジアミン(l)	1.55	カプロラクタム (o)	3.0	5.1	2.0	138	28.0
	ステアリン酸(h)	0.05								
	イソフタル酸(i)	0.50								
15	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(m)	1.55	カプロラクタム (o)	3.0	0.6	4.7	98	93.0
	ステアリン酸(h)	0.05								
	ドデカンジ酸(j)	0.50								
16	ステアリン酸(h)	0.05	メチルペンタ メチレンジアミン (n)	1.55	カプロラクタム (o)	3.0	3.2	3.7	94	100.0
	ジメチル(k) テレフタレート	0.50								
	ドデカンジ酸(j)	1.00								

Key: a) acid; b) diamine; c) additive; d) viscosity; e) example; f) quantity in mols; g) sebacic acid; h) stearic acid; i) isophthalic acid; j) dodecanedioic acid; k) dimethyl terephthalate; l) trimethyl hexamethylene diamine; m) hexamethylene diamine; n) methyl pentamethylene diamine; o) caprolactam

[0058]

[Table 6]

	(a) 酸		(b) ジアミン		(c) 添加剤		AZ	SZ	R+B	粘度(d)
(e) 例	モル量(f)								°C	220 °C Pa·s
17	ステアリン酸(g)	0.05	ヘキサメチレン ジアミン (n)	1.55	カプロラクタム (o)	3.0	0.8	3.7	124	100.0
	ドデカンジ酸(h)	0.50								
	アゼライン酸(i)	1.00								
18	セバシン酸(j)	0.50	ヘキサメチレン ジアミン (n)	1.55	カプロラクタム (o)	3.0	1.6	4.4	92	89.0
	ステアリン酸(g)	0.05								
	ドデカンジ酸(h)	0.50								
	アゼライン酸(i)	0.50								
19	セバシン酸(j)	1.00	ヘキサメチレン ジアミン (n)	1.56	カプロラクタム (o)	3.0	0.7	1.4	140	54.0
	ステアリン酸(g)	0.08								
	イソフタル酸(k)	0.25								
	1, 4-シクロ ヘキサジカルボン酸(l)	0.25								
	ジカルボン酸(m)									

Key: a) acid; b) diamine; c) additive; d) viscosity; e) example; f) quantity in mols; g) stearic acid; h) dodecanedioic acid; i) azelaic acid; j) sebacic acid; k) isophthalic acid; l) 1,4-cyclohexane; m) dicarboxylic acid; n) hexamethylene diamine; o) caprolactam

[0059]

[Table 7]

	(a) 酸		(b) ジアミン		(c) 添加剤		AZ	SZ	R+B	粘度(d)	
(e) 例	モル量(f)								°C	220 °C	Pa·s
20	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(k)	1.55	カプロラクタム (l)	3.0	0.6	2.8	91	80.0	
	ステアリン酸(h)	0.05									
	イソフタル酸(i)	0.45									
	Prilpol (登録商標)(j)	0.05									
	1013										
21	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(k)	1.57	カプロラクタム (l)	3.0	0.7	3.9	109	25.7	
	ステアリン酸(h)	0.07									
	イソフタル酸(i)	0.50									
22	セバシン酸(g)	1.00	ヘキサメチレン ジアミン(k)	1.50	カプロラクタム (l)	3.0	0.4	1.5	112	85.0	
	イソフタル酸(i)	0.45									
	Prilpol (登録商標)(j)	0.05									
	1013										

Key: a) acid; b) diamine; c) additive; d) viscosity; e) example; f) quantity in mols; g) sebacic acid; h) stearic acid; i) isophthalic acid; j) (trademark); k) hexamethylene diamine; l) caprolactam

[0060]

[Table 8]

TABLE 2

番号 (a)	第1表の 例 (b)	方法 (c)	μ での粒子画分 (d)	盛上げ印刷物の表面 (e)	
				外 見 (f)	状 態 (g)
1	1	A	80 ~ 200	極めて均一な、 (h) つや消しの黒色 球構造体	高い耐引掻き性、 (i) 極めて良好なつかみ易さ、 極めて良好な接着
2	1	B	"	"	"
3	2	A	"	"	"
4	3	"	"	"	"
5	4	"	"	"	"
6	5	"	"	"	"
7	6	"	"	"	"
8	7	"	"	"	"
9	8	"	"	"	"
10	9	"	"	"	"
11	10	"	"	"	"
12	11	"	"	"	"
13	12	"	"	"	"
14	13	"	"	"	"
15	14	"	"	"	"
16	15	"	"	"	"
17	16	"	"	"	"
18	17	"	"	"	"
19	18	"	"	"	"
20	19	"	"	"	"

Key: a) number; b) example from Table 1; c) procedure; d) size fraction in terms of μ ; e) surface of raised prints; f) appearance; g) properties; h) very uniform, matted black bead texture; i) high scratch resistance, easy-grip, very good adhesion

[0061]

[Table 9]

番号 (a)	第1表の 例 (b)	方法 (c)	μ での粒子画分 (d)	盛上げ印刷物の表面 (e)	
				(f) 外 見	(g) 状 態
21	1	A	< 63	(h) 極度に微細な球状造体； 十分な構造体効果の形成	耐引掻き性 良好； (k) つかみ易さ 僅か
22	1	"	300 ~ 400	極めて粗い構造体； (i) 個別のより大きく平らな 溶解した樹脂薄膜； 不均一な構造体	"
				(j) 接着温度 °C	ペルクロルエチレン安定性 (l) N / 5 cm
23	20	C	300 ~ 400	140	36
24	21	C	300 ~ 400	140	38
25	22	C	300 ~ 400	140	45

Key: a) number; b) example from Table 1; c) procedure; d) size fraction in terms of μ ; e) surface of raised prints; f) appearance; g) properties; h) extremely fine bead texture, formation of sufficient texture effect [sic]; i) very coarse texture, occasional large-area molten resin films, nonuniform texture; j) bonding temperature; k) good scratch resistance, less pronounced easy-grip property; l) perchloroethylene stability